NASA TECHNICAL TRANSLATION NASA TT F-15,919

VARIOUS METHODS FOR EVALUATING SPECTRA IN QUANTITATIVE SPECTROCHEMICAL ANALYSES

H. Kaiser

Translation of "Über die verschiedenen Verfahren zur Auswertung der Spektren bei quantitativen spektrochemischen Analysen," Spectrochimica Acta, Vol. 2, 1941, pp. 1-17

(NASA-TT-F-15919) VARIOUS METHODS FOR EVALUATING SPECTRA IN QUANTITATIVE SPECTROCHEMICAL ANALYSES (Kanner (Leo) Associates) 27 p HC $4.50 CSCL 07D

N74-31599

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 SEPTEMBER 1974

STANDARD TITLE PAGE

1. Report No. NASA TT F-15,919	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle VARIOUS METHODS FOR EVALUATING SPECTRA IN QUANTITATIVE SPECTROCHEMICAL ANALYSES		5. Report Date September 1974 6. Performing Organization Code
7. Author(s) H. Kaiser, Zeisswerk, Jena		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates, P.O. Box 5187, Redwood City, California 94063		11. Contract or Grant No. NASw-2481 13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION, WASHINGTON, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Über die verschiedenen Verfahren zur Auswertung der Spektren bei quantitativen spektrochemischen Analysen," Spectrochimica Acta, Vol. 2, 1941, pp. 1-17.

16. Abstract The present work gives a review of the various procedures which can be used in exact spectrochemical analyses to evaluate photographed spectra. First we discuss the method of evaluation which depends on the use of internal standards using density differences, and whose range of applicability can be extended considerably using Seidel's extension of the blackening curve. Then the principles of procedures without the use of internal standards are discussed, which are based on the measurement of the true intensity relations between analysis lines. Both for the complete, as well as for the simplified methods, protocols are given that can be used in routine analyses. The bridging of large differences in wavelengths using a bridge spectrum is extensively explained; finally, we show that the free procedures are superior in accuracy to the dependent ones.

17. Key Words (Selected by Author(s))	18. Distribution Statement
	Unclassified - Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	25	

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VARIOUS METHODS FOR EVALUATING SPECTRA IN QUANTITATIVE SPECTROCHEMICAL ANALYSES

H. Kaiser
Zeisswerk, Jena

The following treatise gives a complete review of the various possibilities available to evaluate spectra in quantitative spectrochemical analysis and to determine quantitatively the composition of the samples. Although it contains nothing fundamentally new it seems, nevertheless, justified because the inherent connection between various methods is not immediately obvious from individual publications, since they often differ considerably in their presentation. Therefore, special emphasis was placed on a unified and simple notation which makes the logical connections immediately apparent. Unnecessary concepts and words, such as opacity, transparency, were avoided. The form in which individual methods for evaluation are presented were dictated by the requirements of routine analyses, which must be performed rapidly and without too many mental or mathematical manipulations. /1*

The emphasis of the present work is placed on the presentation of methods for the measurement of the true intensity relationships of the lines obtained in spectral analyses, since they present the basis of the more important method without the use of internal standards, which will doubtless be used more and more in the future. The use of internal standards of known composition for each individual photograph was probably often preferred because it is so plain and conceptually simple and is monitored by the behavior of the sample spectra. It has thereby contributed considerably to the widespread use of quantitative spectrochemical analysis, especially in Germany. It should be remembered that Gerlach and Schweitzer gave the impetus for the newer development with a spectrographically still very simple

*Numbers in the margin indicate pagination in the foreign text.

internal-standard-free method using homologous pairs of spectral lines, and that G. Scheibe et al., soon after the introduction of accurate methods of photometric measurements also gave methods of evaluation without the use of internal standards, and thereby made headway in the direction that will be taken in the future. The various methods of evaluation are based on the properties of photographic plates which allow relating the degree of blackening to the intensity of the light to which they were exposed. We start, therefore, with a brief discussion of the plates. /2

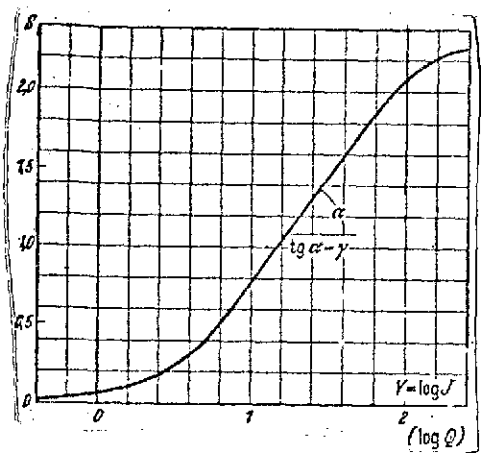

Fig. 1. Blackening curve of a photographic plate (schematic).

1. Density Measurements of Photographic Plates

a) The Concept of Blackening

The spot on a plate which was exposed to light is blackened during development due to reduction of the silver. "Blackening" is the measure of the density of reduced silver which is determined in a photometer. On the assumption that reading A on the scale of the photometer is proportional to the light that goes through the blackened places on the plate, the blackening S is defined in the following way:

$$S = \log \frac{A^\circ}{A}$$

A° represents the reading of a clear, unblackened place on the plate.

The density difference ΔS for a spectral line of an added element Z relative to a base element G gives the following relation from the photometer readings:

$$\Delta S = S_Z - S_G = \log \frac{A_G}{A_Z}.$$

The reading of A° for an unblackened place on the plate thereby cancels out.

b) The Blackening Curve

The blackening curve gives the relationship between the density S of a given spot on the plate and the amount of light, Q, to which this spot was exposed. The curve is shown in Fig. 1; the density S is plotted on the vertical axis, the log of the incident light, Q, is plotted on the horizontal axis (e.g. measured in W-sec). The curve is S-shaped; on hard-working photomechanical plates it becomes nearly linear in the middle range; with some other types of plates, it remains continuously curved. Inclination and sag of the curve are strongly dependent on the wavelength of the incident light and the method of developing. The tangent to the angle of inclination in the middle (linear) portion of the curve is called the "steepness" or gradation of the plate and is symbolized by the letter gamma.

We postulate that for any given set of photographs the exposure time and the light transmission from the light source to the plate are constant. Then the amount of light, Q, (i.e. the radiation yield per unit of solid angle in W) is proportional to the intensity J in the light source. One can therefore also plot the logarithm of the intensity, log J, on the abscissa in Fig. 1, in which case only the zero point changes when compared to a plot of log Q. In what follows we shall use the abbreviation Y to designate the quantity log J. The way to establish a blackening curve for a given wavelength on a given type plate will be discussed in Section 7.

2. Evaluation Using Density Differences

Every method of quantitative spectrochemical analysis requires calibration using samples of known content. In a method widely used,

especially in Germany, first devised by R.A. Lomakin [1], this calibration is carried out for every single plate separately: in addition to the spectra of the experimental samples, several standard samples of known content are photographed on the same plate. Evaluation of such plates is extremely simple: The density difference ΔS between a given line of the added element Z, which is to be determined, and that of the base element G gives the measurement directly. The density differences for the standard samples are plotted against their respective concentrations k, which gives the calibration curve valid for that particular plate. Using it, the concentrations of the unknown samples can be determined from the measured values of ΔS. It is useful to plot concentrations on a logarithmic scale, because they often given nearly linear calibration curves which are easy to draw and to evaluate. But curved calibration curves are possible and equally useful. Figure 2 shows an example of a calibration curve.

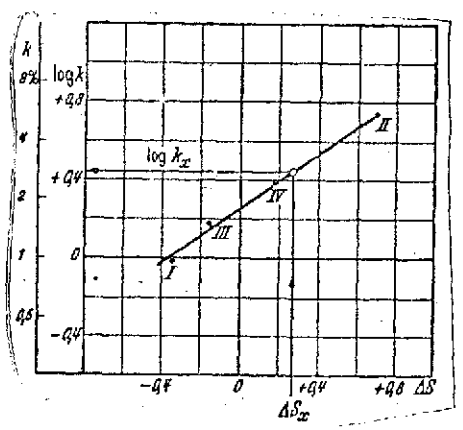

Fig. 2. Example of a calibration curve (schematic). (I through IV are points from standard samples, ΔS_x is the value of the unknown.)

This type of evaluation /4 is useful as long as all densities remain in the linear range of the calibration curve; in this range, the density differences are independent of the magnitude of the blackening itself. Outside of the linear range, the calibration curve deviates from linearity because relatively large concentration changes yield little differences of blackening (Fig. 3). At the same time, the values of ΔS which correspond to a given concentration become dependent on the magnitude of the blackening, so that the position of the curved portions of the calibration curve

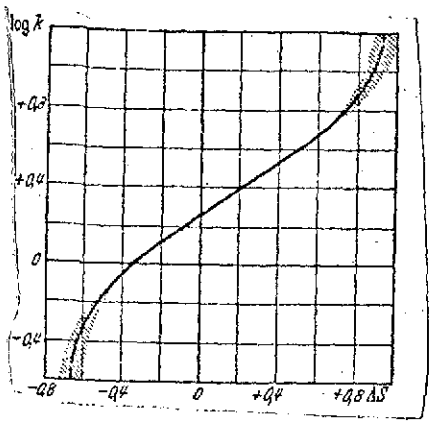

Fig. 3. Complete calibration curve in a ΔS – log k diagram (schematic).

depend on variations in exposure time etc., and become unreliable (which is represented in Fig. 3 by shading).

3. Extension of Applicability When Blackening is Slight

In the range of low densities and, therefore, also low content, the curvature of the calibration curve and the resulting uncertainty can in many cases be prevented by stretching the lower part of the blackening curve of the plate by means of a mathematical transformation given by W. Seidel.[1] We designate the new value as "transformed blackening" T, which can be calculated from the photometric readings in the following way:

$$T = \log\left(\frac{A_0}{A} - 1\right).$$

For intense blackenings, T is approximately equal to S, for low densities, below 0.3, T becomes negative. Figure 4 shows a density curve and the corresponding straight line of the transformed density T (broken line). Such a completely straight line for T is obtained only if the density curve satisfies an equation of the form $S = \log (1 + \text{const} \cdot 10^{\gamma \cdot Y})$ which will not be generally exactly true. The upper curvature of the density curve is not influenced by the transformation to T, but this is not important for the measurements.

In the analysis, the value of ΔS is replaced by the value $\Delta T = T_Z - T_G$. The calibration curve used in evaluation as described in Section 2 can thus be continued in a linear or nearly linear fashion, such that the useful range of this method for evaluation

[1] Given at a seminar of the Spectroanalytic Committee of the Society for Metal and Ore, July 21, 1939, in Düsseldorf. The author wishes to thank Dr. Seidel for permission to use his suggestion.

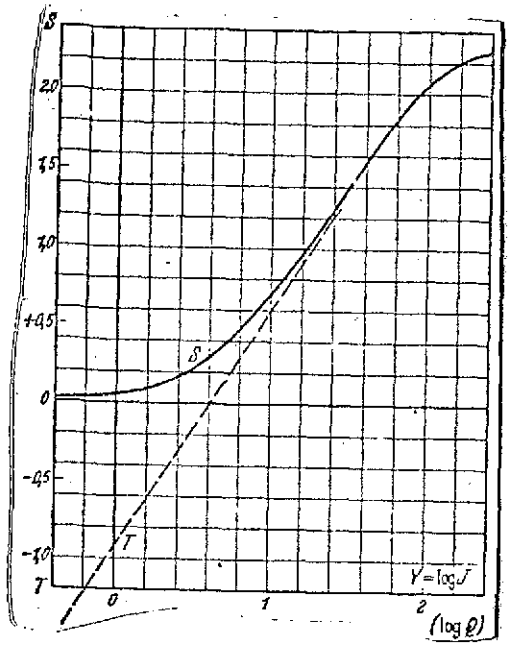

Fig. 4. Seidel's transformation of the density curve.

can be extended into the range of low contents; it can cover several orders of magnitude of concentrations.

4. General Principles of Methods Without the Use of Internal Standards /5

In quick analyses, taking of spectra of standard samples represents a waste of time; furthermore, the method becomes prohibitively expensive through use of accurately analyzed samples which are often difficult to obtain, and the errors in the measurements on the standard samples are carried over into the results of the analyses. For all these reasons the further development of spectrochemical methods of analysis will promote the use of methods in which the taking of standard sample spectra is no longer necessary. Such methods have been known for a long time and will be systematically discussed below.

We presuppose that for a given analytical problem a useful protocol is available, i.e. especially that evaporation of the samples and excitation of certain spectral lines in the light source are carried out in a standardized and reproducible fashion. We suppose further that the conditions within the light source remain constant, not only in the course of one set of experiments, but that a light source with identical characteristics can always be obtained again according to the protocol. For such a light source, the intensity relation of paired analyses is always the same for a given sample. For a similar sample of different content of the added element Z, a different but equally reproducible intensity relation is obtained.

In "samples" of the same kind there exists, using the appropriate light source, and independent of any measurement, a certain, constant relationship between the content of the added element Z and the intensity relation of the paired lines in the analysis.

This immutably given relation between the intensity relation and the content has to be determined once for all through "standardization of method" (rather than calibration of plates) using external standards of known content. This "standardization of method" yields the "master standard curve" which serves as the basis for all subsequent analyses; the standard samples have thereby served their purpose and need not be used again in the individual analyses.

Here, as well as in what follows, we distinguish between "internal standards" which are used in an individual analysis in constructing the specific calibration curve, and the "external standards" which are used to establish the generally valid master standard curve of the method. The internal standards accompany the unknown sample throughout the whole procedure, whereas the external standards have been established some time, some place. There are no procedures of quantitative spectrochemical analysis without calibration standards, but there are methods without internal standards. These will be referred to simply as "free methods" as opposed to the "dependent methods" (internal standards). W. Gerlach designated the free methods as "absolute" methods; we do not want to use this word, in order to make quite clear that there is no truly absolute, i.e. calibration-standard-free method.

In each individual free analysis it is important to measure the intensity relation between paired lines of the analyses. When a photographic plate is used as radiation acceptor -- which is most often the case -- the intensity relation has to be determined /6 from the blackening of the lines using blackening calibration curves.

We designate the logarithm of the intensity relationship, $\log J_Z/J_G = Y_Z - Y_G$ by ΔY. This value plays a similar role in the free methods as the blackening difference ΔS in the usual evaluation.

5. The Course of Complete Evaluation in the Free Methods

We suppose that the blackening curve of a given plate (S vs. Y, Fig. 5a) and the master calibration curve of the procedure (log k vs. Y, Fig. 5b) are given. How, then, is the concentration determined from the measured densities S_Z and S_G from the pair of analyses?

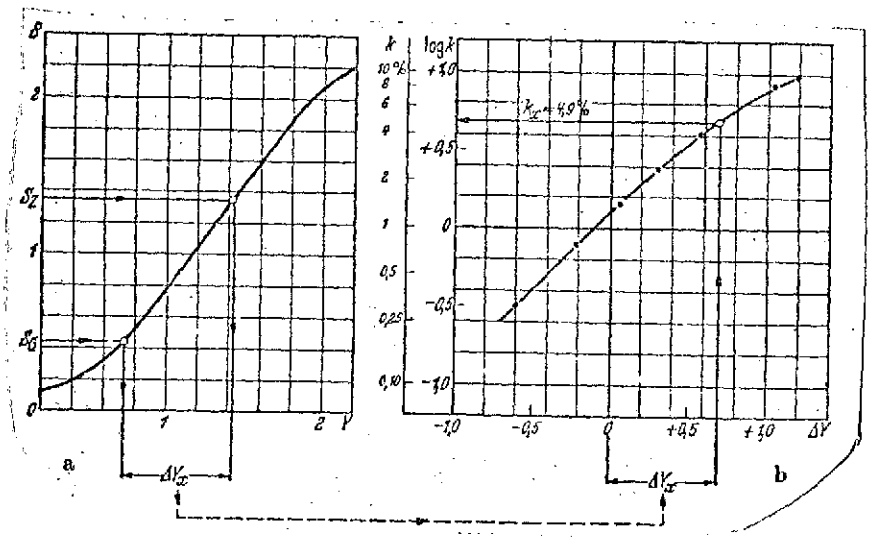

Fig. 5. Complete evaluation for the procedure without internal standards. a) Blackening curve of the photographic plates; b) generally valid master calibration curve.

One finds the values of S_Z and S_G on the density scale in Fig. 5a and goes from there horizontally to the blackening curve, from which one goes vertically to the abscissa. The space that lies between the bottom points on the abscissa gives Y_x, the

logarithm of the intensity relationship for the unknown sample x. (Whenever the line of the added element is blacker than the line for the base element (S_Z larger than S_G), ΔY is positive, otherwise it is negative.)

The value of ΔY thus found is now transferred, with its proper sign, to the ΔY scale of the master calibration curve Fig. 5b starting from the zero point on that scale. From the end point of that transferred value, one constructs a perpendicular line to the Y axis, and where that vertical line intersects with the calibration curve one goes horizontally over to the ordinate, where one locates the value of log k, the logarithm of the concentration to be determined.

This evaluation is easily carried out according to Owens [2] if, instead of the master calibration curve, a movable number scale is used which one can lay along the horizontal axis of the blackening curve (Fig. 5a). This number scale is nothing but the ΔY scale of Fig. 5a, except that the points do not represent the values of ΔY but that of the concentration to which they correspond according to the calibration curve.

The zero point on the old ΔY scale is marked with a locating mark. Figure 6a shows how the concentration curve is derived from the master calibration curve. Figure 6b shows its utilization. It is to be laid on the abscissa of the blackening curve such that the locating mark lies below the Y-value of the line for the base element. The perpendicular of the Y-value on the line for the added element gives the concentration that was to be found, k_x. Owens [2] has described an abacus which permits rapid and easy evaluation; Figure 7 shows such an abacus according to Vincent and Sawyer [3]. The blackening curve is to be seen on the paper, the transparent ruler is used to construct the perpendicular of the measured values, and below on the movable slide are several concentration scales.

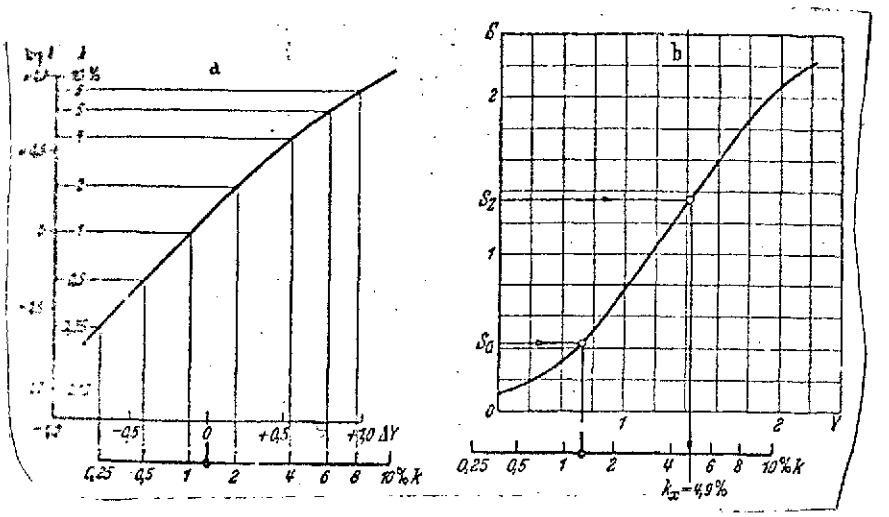

Fig. 6. Complete evaluation using an abacus.
a) Derivation of the concentration scale from the master calibration curve.
b) Application of the scale in connection with the density curve of the photographic plate.

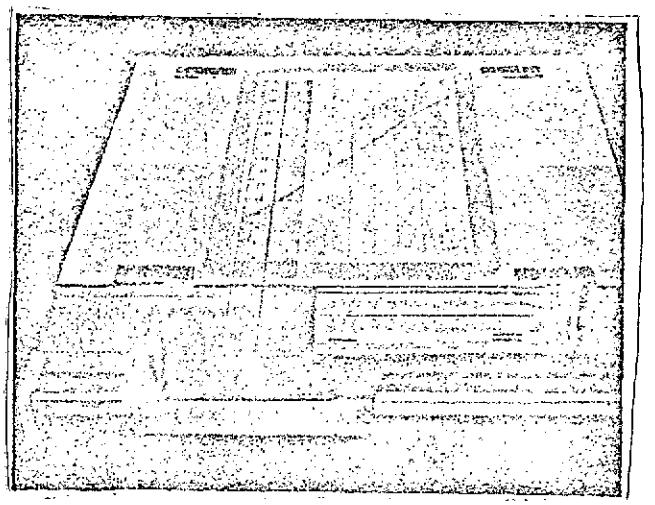

Fig. 7. Evaluating apparatus.

6. Standardization of the Method

In order to establish the generally valid, unchangeable proportionality between the intensity relation (measured as ΔY) and the concentration k, photographs have to be taken, according to protocol, of several samples of accurately known content and in appropriate gradations. In these spectra the blackenings S_Z and S_G of both lines are measured and the values of ΔY are determined using the blackening curve. The respective values of k or log k and ΔY give, when plotted on a coordinate system, several points of the calibration curve which can then be drawn. Through averaging over

several such calibration photographs errors of measurement can be so minimized that adventitious errors in the calibration curve will always be insignificant compared to errors of measurement in subsequent individual analyses. /8 Systematic or random errors which occurred in the determination of the contents in the samples used to establish the calibration curve cannot in this way be eliminated. It is therefore mandatory that the contents of the samples used for standardization be determined reliably.

7. Determination of the Blackening Curve

We shall now discuss the best way to determine the blackening curve of individual plates. For this purpose a series of intensity markers is used, the intensity relation of which is known (ΔY) and using them one can now establish the proportionality between relative intensities and blackening. How can one photograph markers of accurately known intensity relations?

Reliable measurements of photographic intensity can generally only be made by holding all experimental conditions, especially time of exposure, kind of lighting and the wavelength of the light constant, whereas only the intensity of the photographs to be compared is varied. These are strict requirements, and a blackening curve that was established using continuous light is not valid for the discontinuous light of a series of flashes. There are four different possibilities to obtain intensity markers that fulfill these requirements:

a) Calibrated, graded filters, which are put in front of the slit of the spectrograph. Transmittance through such filters is generally dependent on the wavelength and has therefore to be determined for the particular wavelength to be used in the ultimate measurements. In the UV, filters of vaporized platinum are particularly useful because their transmittance changes only little with wavelength.

b) Step-light stops with graded apertures, which are so arranged that various sections of the slit in the spectrograph are exposed to light beams at different angles of aperture, which correspond to individual sections of the light-stop. To accomplish this, cylindrical lenses have to be inserted into the light beam before it reaches the slit; W. Kinder [4] has given an overview of the various possibilities available.

c) Graded slit. In this case the slit of the spectrograph consists of several sections of different widths. On exposure to a light source of continuous wavelengths (continuous spectrum), /9 the light beam which hits a given spot on the plate is, as long as the slits are not too narrow, proportional to the slit width. This procedure was first reported by Vierordt [5] and was used in spectrochemical measurements by K.B. Thomson and O.S. Duffendack [6]. When using intensity markers that were obtained with a light source of continuous spectrum for measurements of line spectra, one must be especially aware of interferences by photographic development effects (Eberhard-effect).

d) Sets of chosen spectral lines of small differences in wavelength and accurately measured intensity relations. This possibility of measuring the blackening curve of a plate does not require special accessories if the intensity relation of the lines has been measured first by one of the procedures (a-c). This procedure is especially recommended when the base element of the sample to be analyzed has a sufficiently rich line spectrum as, for example, iron does. In selecting the lines one must be careful that the intensity relationships be insensitive to variations in the light source.

Besides the possibilities discussed above, the logarithmic sector or step-sector is much in use, especially in American work; it had first been used in spectrochemical analyses by G. Scheibe

and A. Neuhäusser [7] to obtain graded intensity markers. Sectors, however, do not give a graded intensity but graded time of exposure; in addition, they produce interrupted exposure. The blackening curves obtained using sectors do not generally coincide with those obtained using true intensity filters (a-d), i.e. one cannot make true intensity measurements using sectors. The opinion that blackening curves obtained using sectors are, indeed, usable in accurate intensity measurements, provided only that the number of revolutions per unit time of the sector is high enough does not appear to be generally true according to newer investigations [8, 9]. For comparative measurements, however, where a totally reliable intensity measurement is not necessary, sectors are a very convenient photometric accessory. (G.R. Harrison [10] has given a systematic review of the various procedures of photographic photometry.)

It is useful to prepare a piece of graph paper in the manner shown in Fig. 8a in order to be able to draw the blackening curve quickly during the valuation. On points a, b, c, etc. on the Y-axis perpendiculars are drawn which correspond to the relative intensities of the chosen markers. In the course of measuring, one plots on these perpendiculars the blackening values S_a, S_b, S_c, etc. of the corresponding markers which are individual points of the blackening curve which one merely connects in the end (Fig. 8b).

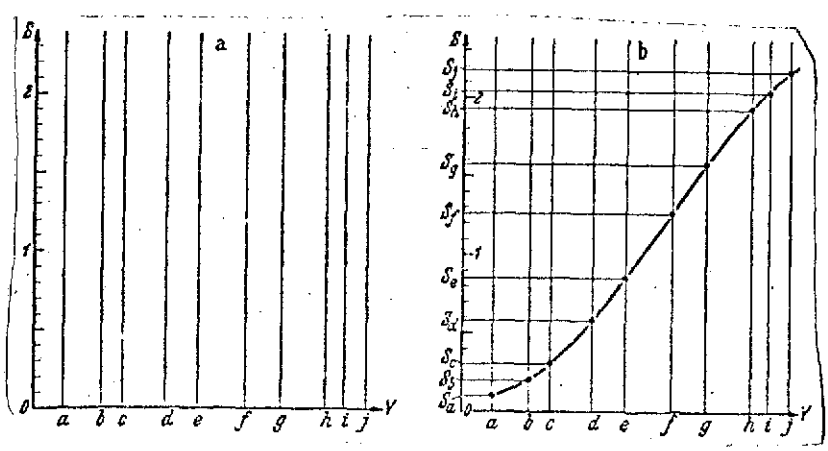

Fig. 8. Drawing of the blackening curve. a) Prepared graph paper; b) curve drawn.

We wish to mention that any univalent function of S can be /10
used to construct a characteristic curve, e.g. with the transformed blackening T which often gives a linear curve. If the reading on the photometer is held constant for the unexposed plate, the meter reading A itself can be plotted. In some American investigations the value $(A_o - A)$ is used, where the reading A_o is set equal to 100 divisions on the scale. This value is referred to by some authors, e.g. Owens, as "blackening" whereas others use "density" for the same word, interchangeably.

When using a photometer with a log scale (see E. Preuss [11]), where the reading gives log A immediately, one can use these values without further manipulations; one obtains a curve which coincides with the usual blackening curves exactly, only the zero point on the ordinate is moved by the constant value of A_o. Which of these possibilities one is to choose is dictated by simplicity of procedure in industrial analyses. In any case, a mathematical workup of the readings is to be avoided. It is not even necessary to write the readings down; they can be plotted immediately and the time thus saved can be of importance in rapid analyses.

8. Simplified Methods Without the Use of Internal Standards in the Linear Range

The complete evaluation as described in Section 5 can be simplified considerably if one limits oneself to the linear portion of the blackening curve. In this range the density difference ΔS of two lines is proportional to the logarithm of their intensity relation ΔY. From Fig. 1 we see immediately that $\Delta S = \gamma \cdot \Delta Y$. To determine the value of γ, one only needs two intensity markers of known ΔY. (We designate the values of the markers with the index m.) The density difference ΔS_m of the two markers is /11
measured on the plate. Then γ is given by

$$\gamma = \frac{\Delta S_m}{\Delta Y_m}.$$

Thereby the intensity relation corresponding to each blackening difference ΔS in the linear range can be determined according to the equation

$$\Delta Y = \left(\frac{\Delta Y_m}{\Delta S_m}\right) \cdot \Delta S.$$

The value thus determined of ΔY for a pair of lines can be plotted on the master calibration curve.

Evaluation becomes particularly simple if the master calibration curve of log k vs. ΔY is completely linear or, at least is linear over a considerable range. Then the equation assumes the form:

$$\log k = \log k_0 + p \cdot \Delta Y,$$

where log k_o, and p are constants. Substituting the value of ΔY_x from the previous equation, one obtains:

$$\log k_x = \log k_0 + p \cdot \frac{\Delta Y_m}{\Delta S_m} \cdot \Delta S_x.$$

When the constants k_o, p, ΔY_m in this equation are known, one only needs the density difference of the markers and of the line pair of the analysis for evaluation of a photograph. It is not even necessary to know the intensity relation of the two markers exactly; because when using the above equation for the photograph of the two samples of known content one can determine k_o and the product $(p \cdot \Delta Y_m)$.[2]

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[2]Numerical example: Sn-determination in a lead alloy using the lines Pb 2657 A and Sn 2661 A. The calibration equation used in this procedure was:

$$\log k = -0.425 + 2.10\ \Delta Y$$

log k_o is therefore -0.425, i.e. the concentration k_o is 0.376%. The slope of the density curve had been determined using a graded filter; its $\Delta Y_m = 0.278$. The density of the Pb line was measured using both filter gradations, that of the Sn line only in one. The following values were obtained: $S_{Pb_m} = 0.925$; $S_{Pb} = 0.579$; $S_{Sn} = 0.01$; therefore:

$$\Delta S_x = 0.231 \text{ and } \Delta S_m = 0.346.$$

[continued on following page]

9. Graphic Evaluation in the Linear Range (Two-Point Evaluation)

The calibration equation can also be solved graphically, which turns out to be especially simple if one proceeds from two precisely chosen ΔS values, namely from $S = 0$ and $S = S_m$. In the first instance, the line of the base element has the exact same density as the added element and the corresponding concentration is k_o. In the second instance the density difference of /12
the lines in the analysis is exactly that between the markers. The corresponding concentration can be calculated from the equation, and it is k_m.

If the values for k_o and k_m have been determined once for all, one only has to measure the density difference ΔS_m of the markers and can immediately draw a calibration curve which is valid for that particular plate. The graph paper for this curve should be prepared as follows (Fig. 9): one draws the coordinates with the scales for log k and ΔS. The point (log k, $\Delta S = 0$) is marked specially. All possible calibration curves have to go through this point. We therefore call it the "fixed point" of this spectrochemical procedure of measurement, as introduced by W. Gerlach. Further, an auxiliary line is drawn through the point (log k_m, $\Delta S = 0$) parallel to the ΔS axis. In evaluating a photograph one first measures ΔS_m and constructs a perpendicular through the point ΔS_m on the abscissa. The point where this perpendicular intersects with the auxiliary line gives the second point of the calibration curve, which can now be drawn. From the measured value S_x of the line pair, the concentration can be determined

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[2] (cont'd)

Substituting all this into the equation, we get:

$$\log k_x = -0{,}425 + 2{,}10 \frac{0{,}278}{0{,}346} 0{,}231 = -0{,}035.$$

The concentration to be determined was $k_x = 0.92\%$.

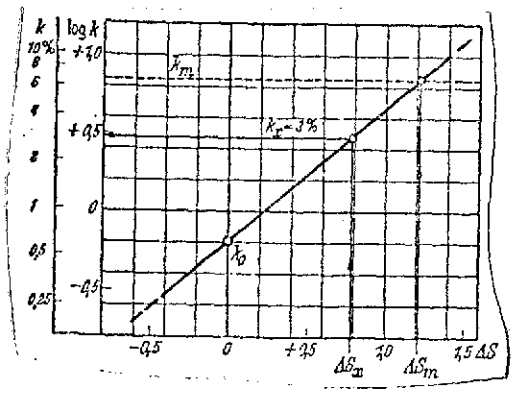

Fig. 9. Two-point evaluation (k_o, 0) = the fixed point. k_m = auxiliary line.

determined, as is demonstrated in Fig. 9.[3]

We designate the graphic evaluation in the linear range "two-point evaluation"; it was first given by G. Scheibe and O Schnettler [12]. Two lines, G_1 and G_2 of the base element were used as intensity markers, one of which was at the same time the reference line for the added element. One thus needs three lines; therefore, the name "three-line procedure." Later G. Scheibe and A. Schöntag [13] produced the intensity markers using a two-step filter. One line of the base element was measured in both gradations of the filter and thus gave the value of ΔS_m. Therefore, this procedure got the name "two-line procedure." It has the added advantage that it is usable over a wide concentration range because the whole spectrum is available in two gradations from which one can always select the one which lies in the proper range of blackening.

10. Bridging of Larger Differences in Intensity and Wavelengths

The above-mentioned simplified procedures presuppose that the differences in intensity between the two lines of an analysis pair are not too great, such that both densities lie within the linear range of the blackening curve. But even in cases where /13 one would use the entire blackening curve, very large density differences cannot be determined with sufficient accuracy. In

[3] In lieu of the two ΔS values one can also use the three blackenings S_g, S_z and S_m directly. In lieu of the point (log k_o, ΔS = 0) one then needs an auxiliary line through k_o. Both ways are about equally convenient to carry out; the one given in the text emphasizes the logical connections particularly clearly.

such cases one needs to put a two-step or variable-step filter in front of the slit of the spectrograph. One then measures the lighter line using a lighter gradation of the filter, the stronger one using a darker gradation. When all photographs to be compared are made with the same filter, the transmittance of the various filter gradations need not be known; it is sufficient to know that they are invariant. All intensity relations determined then contain an unknown but constant factor.

Large differences in wavelength between the lines to be measured cause more serious difficulties. Because the sensitivity and slope of the plates are generally strongly dependent on the wavelength, such that accurate intensity measurements according to previously described methods are only possible when the same blackening curve is valid for both wavelengths. In the much used UV range between 2400 and 3300 A, the slope of the blackening curve is, fortunately, independent of the wavelength for most plates, so that in this range lines that are relatively far apart can be compared. In other ranges of the spectrum, especially in the near-UV, where the slope changes considerably with differences in wavelength, the differences in wavelength must be bridged using an auxiliary spectrum. We shall call the auxiliary spectrum a "bridge spectrum." It must satisfy the following conditions:

a) In the immediate neighborhood of the wavelengths of the lines for Z and G which are to be measured in the experimental spectrum, two lines B_Z and B_G must lie in the bridge spectrum and must be of comparable strength as the corresponding lines of Z and G.

b) It must be possible to reproduce the bridge spectrum of given characteristics; especially the intensity relation J_{BG}/J_{BZ} of the two chosen lines in the bridge spectrum must have a certain constant value.

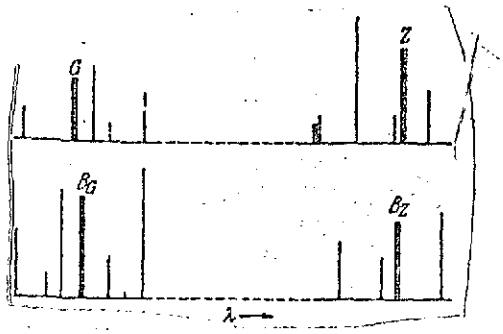

Fig. 10. Bridging of differences in wavelengths. Above: sample spectrum with the lines Z and G. Below: bridge spectrum with auxiliary lines B_Z and B_G (schematic).

As bridge spectrum one can take that of an ordinary lamp, e.g. of a platinum lamp ((Osram) or that of a black body or the spectrum of a pure metal. It is especially convenient to take as bridge spectrum that of a certain sample of the kind to be analyzed exactly according to protocol. The two analysis lines Z and G in this spectrum can then be used as the bridge spectrum.

Figure 10 depicts the sample and bridge spectrum schematically. The vertical lines represent the various lines, their length indicates the intensity; the four lines which are measured are thickly drawn. /14

In evaluations using bridge spectra, the two density curves which are valid for the wavelengths of Z and G are first determined. Thereby one can determine the intensity relation of each line analysis and its corresponding bridge line, thus:

$$J_Z/J_{BZ} \text{ and } J_G/J_{BG}$$

as discussed in Section 5. Now the following relation holds:

$$\frac{J_Z}{J_G} = \frac{J_Z}{J_{B_Z}} \cdot \frac{J_{B_G}}{J_G} \cdot \left(\frac{J_{B_Z}}{J_{B_G}}\right)$$

or in logarithmic notation:

$$\Delta Y_{Z,G} = \Delta Y_{Z,B_Z} - \Delta Y_{G,B_G} + \text{const.}$$

If, therefore, the blackening curves for the wavelengths of Z and G are known, the intensity relation of the line analysis can

then be determined from four density measurements, except for a constant factor. In spectrochemical determinations it is usually not necessary to know the numerical value of this factor; it suffices to know that it is constant.[4]

This measuring procedure as such has long been known; see, e.g. Ornstein, Moll and Burger [14]. In applications to spectrochemical analyses it has been referred to as the "method of the

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[4] Numerical example: The intensity relation of the zinc line 2335 A and of the lead line 2400 A in the spectrum of a lead alloy is to be determined. The slope of the blackening curve is 53.5° at 2400 A, and $\gamma = 1.35$; at 2335 A the slope is 42°, $\gamma = 0.90$. Therefore, an immediate density measurement is not possible. Then spectrum of a certain lead alloy of the same kind is therefore taken as bridge spectrum; the Sn and Pb lines in this spectrum serve as bridge lines. The measurement gives, for the analyzed spectrum:

$$S_{Sn} = 0.889 \text{ and } S_{Pb} = 1.101$$

for the bridge spectrum:

$$S_{Sn_B} = 0.482 \text{ and } S_{Pb_B} = 1.018.$$

The density difference for the lines at 2335 A is

$$\Delta S_{Sn} = 0.407$$

that for the lines at 2400 A is

$$\Delta S_{Pb} = 0.083.$$

The corresponding intensity relations are given from the γ values from the formula:

$$\Delta Y = \frac{\Delta S}{\gamma}$$

$$\Delta Y_{Sn} = \Delta Y_{Z,B_Z} = 0{,}452$$

$$\Delta Y_{Pb} = \Delta Y_{G,B_G} = 0{,}062.$$

The difference between both these values gives the logarithm of the intensity relation to be determined, except for a constant, such that

$$Y_{Sn,Pb} = 0.390 + \text{const.}$$

external standard" especially in American investigations (see J.T.M. Malpica [15]).

We wish to mention one other way to bridge large differences /15 in wavelengths, which is especially useful in the far UV. This is to transform the incident, heterochromatic light into monochromatic light. For this purpose, the plate is covered with a thin film of fluorescent material, for instance with mineral oil. This film must absorb all incident light such that only the fluorescent light can affect the plate. Furthermore the light transformation must follow an unchanging law, otherwise it cannot be used in intensity measurements. There are materials, as G.R. Harrison and P.A. Leighton have noted in investigations with mineral oil and pure Aesculin [16], whose fluorescence yield is constant over a wide range of wavelengths (2000 to 3900 A), i.e. the intensity of the fluorescent light is proportional to the product of the incident light and its wavelength. Production of such fluorescent plates is, however, not simple, because the appropriate and even thickness of the film is important [17]; furthermore, one must ascertain whether the law of light transformation can be used.

11. Accuracy

We now wish to discuss how the accuracy compares in free and dependent procedures. As an example, we compare two analyses of the same kind in which the linear range of the calibration curve is to be established: In the free procedure the concentrations k_o and k_m are given by the generally valid calibration curve, in the dependent procedure two internal standards I and II of concentrations k_I and k_{II} are taken. We suppose that the values of k_o, k_m, and k_I and k_{II} are exactly known. The samples used as internal standards have been analyzed accurately and standardization of the procedure has been done in sufficient

numbers that all random errors have been sufficiently minimized. Then, any errors in the analysis are due only to errors in the measurements of the density differences. In the free procedure we measure: ΔS_m and ΔS_x; in the dependent one: ΔS_I, ΔS_{II} and ΔS_x. The free procedure contains one less measurement and therefore one less possible source of error; furthermore, ΔS_m is subject to a smaller error than all other ΔS values, if the intensity markers were produced with a filter; because all disturbances which arise from the light source and the sample have been eliminated, the only source of error remains the plates and the photometer itself.

Carrying out all calculations, we arrive at the following result: we designate the average error in log k as analysis error, m_A, the part of the average error in ΔS values, due to the light source, m_L, that due to the plate and the photometer, m_p. Furthermore, let a be the tangent to the slope of the calibration curve and b the relation of the two portions into which the measured point of the sample cuts the line between the calibration points in the log k - ΔS plane. Then the error of the analysis for the dependent procedure is:

$$m_{A_{dep.}} = a\sqrt{2\,(1+b^2-b)\,(m_L^2+m_P^2)}$$

and for the free procedure: /16

$$m_{A_{free}} = a\sqrt{(1+b^2)\,m_P^2+m_L^2}$$

The difference between these two errors is always positive, i.e. the free procedure always gives the smaller deviation for the values of analysis.

We wish to illustrate these formulas for the determination of standard errors with a numerical example: Let the slope of

the calibration curve be 40°, i.e. a = 0.84, k_I in the dependent, k_x in the free procedure by 2%, k_{II} and k_m be 8%, the concentration in the sample to be analyzed be in the range of 4%. Then the measured point of this sample lies exactly mid-way between the two calibration points: b = 0.5. This is the best case for the dependent method, because the term under the first radical has a minimum value.

For the average errors due to the light source and photometry, we choose values that are obtained with excellent procedures: m_p = 0.004 and m_L = 0.010. Substituting these into the formulas, we find:

$m_{A_{dep.}}$ = 0.0111, corresponding to 2.6% of the content,

$m_{A_{free}}$ = 0.0092, corresponding to 2.14% of the content.

If the content of the unknown sample lies closer to the fixed point, k_o, e.g. 2.6%, the comparison is even more favorable for the free method. Then we have b = 0.2 and the error in the dependent analysis would be 2.73%, that in the free method, 2.11%.

The free procedure is thus recommended not only because of economy in time and sample material, but also because of its greater accuracy, provided that the prescribed conditions can always be reproduced.

We have limited ourselves in this review to a discussion of methods of evaluation to be used in conjunction with accurate photometric measurements of photographic plates. It is, however, the use of these plates qua radiation acceptors which complicates these procedures. The principle which was applied throughout in this discussion can, however, be extended to procedures of lesser requirements in photometry and leads then to a systematic ordering of all procedures of evaluation in quantitative spectrochemical methods. The fundamental thoughts in this ordering are:

1. Division into free and dependent procedures.

2. Arrangement in order of decreasing requirements of accuracy in photometry.

In this classification the method using homologous line pairs in the free procedure and intercalation of the spectrum of an unknown sample into comparative spectra in the dependent method are set side by side. These two procedures are on the same photometric level: the judgment of equality of blackening by eye. On the lowest level of a "photometric hierarchy" would be determination of the "last lines," in which the threshold value of the whole apparatus is used in photometry.

Such a classification delimits the various procedures /17
with respect to accuracy, dependability and useful range in order to facilitate a choice of the most appropriate method for a given analytical problem.

REFERENCES

1. Lomakin, R.A., Z. anorg. u. allg. Chem. 187, 75 (1930).
2. Owens, J.S., Metals and Alloys 9, 15 (1938).
3. Vincent, H.B. and R.A. Sawyer, Metal Progress 36, 35 (1939).
4. Kinder, W., Z. Instrumentenkde 56, 393 (1936).
5. Vierordt, C., Pogg. Ann. 140, 172 (1870).
6. Thomson, K.B. and O.S. Duffendack, J. Opt. Soc. Amer. 23, 101 (1933).
7. Scheibe, G. and A. Neuhäusser, Z. angew. Chem. 41, 1218 (1928).
8. Strock, L.W., Spectrochim. Acta 1, 123 (1939).
9. Kienle, H., Naturwiss. 23, 759, 762 (1935).
10. Harrison, G.R., J. Opt. Soc. Amer. 24, 59 (1934).
11. Preuss, E., Z. angew. Mineral. 1, 172 (1938).
12. Scheibe, G. and O. Schnettler, Naturwiss. 18, 753 (1930); 19, 134 (1931).
13. Scheibe, G. and A. Schöntag, Arch. Eisenhüttenwes. 8, 533, (1934/35).
14. Ornstein, Moll, and Burger, Objective Spektralphotometrie [Objective spectral photometry], Braunschweig, 1932.
15. Malpica, J.T.M., Gen. Electr. Rev. 43, 333 (1946).
16. Harrison, G.R. and P.A. Leighton, Phys. Rev. 88, 899 (1931).
17. Müller, W. and A. Sieverts, Spectrochimica Acta 1, 348 (1940).